

Metal limitation of cyanobacterial nitrogen fixation on the early Earth

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Reduced nitrogen is produced primarily by nitrogen fixing organisms (diazotrophs) that utilize the enzyme nitrogenase, a metallo-enzyme that contains a molybdenum-iron cofactor in its most efficient form. Fluctuations in the bioavailability of such redox-sensitive metals have occurred as the redox state of the oceans has changed with progressive oxidation of the Earth's atmosphere through time. To examine the potential effects of metal limitation on cyanobacterial N₂ fixation, we grew *Anabaena variabilis* str. ATCC 29413 in batch and continuous cultures in Mo- and Fe-limited media. Molybdenum availability strongly affects N fixation rates below initial [Mo] of 5nM, but has little effect on growth rates. Iron availability exerts a strong control on growth rates, with a less dramatic effect on N fixation. The highest heterotrophic growth rates correspond to the lowest N fixation rates in high-Fe low-Mo experiments, where the Fe and Mo concentrations are similar to those predicted for anoxic (i.e. Archean) conditions. Growth is slowest in low-Fe low-Mo experiments, where concentrations are analogous to those estimated for a sulfidic Proterozoic ocean, but nitrogen fixation rates in this case are equal to those in low-Fe high-Mo experiments replicating modern ocean conditions. In autotrophic experiments, growth rates are much slower, but show a similar trend; nitrogen fixation rates are similar but slightly lower in Fe-limited media. These results taken together suggest that an overall decrease in cyanobacterial ammonia production could have occurred in the Proterozoic ocean, primarily due to diminished growth rates rather than lower rates of N₂ fixation.